Grant No. AFOSR-90-0337

An Alternative Approach to the Growth of Single Crystal Gallium Nitride

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30 June 1993

Final Scientific Report 1 Sep 90 - 31 Jan 93

Prepared for

United States Air Force
Air Force Office of Scientific Research
Building 410
Bolling AFB
D.C. 20332-6448

and

European Office of Aerospace Research and Development
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London NW1 5TH

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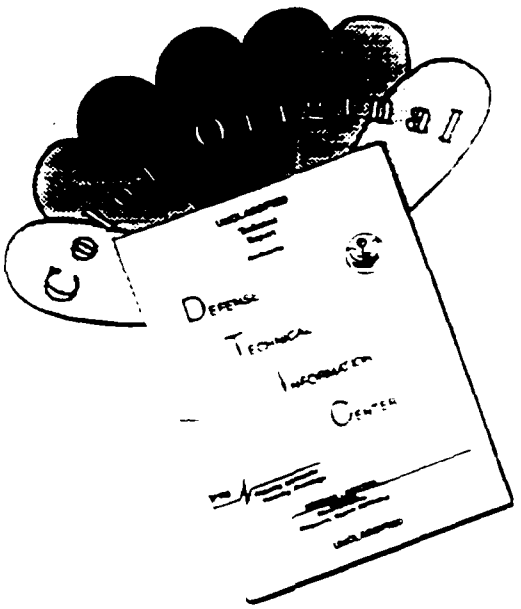

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		Final Technical Report 1/9/90-31/1/93

4. TITLE AND SUBTITLE
An Alternative Approach to the Growth of Single Crystal Gallium Nitride

5. FUNDING NUMBERS
Grant No.
AFOSR-90-0337

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
AFGAN-2

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
EOARD
223/231 Old Marylebone Road
London NW1 5TH

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
TR-93-08

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This project has been primarily concerned with investigating a new approach to the synthesis of epitaxial layers of high purity gallium nitride. The new approach involves the use of hydrazoic acid, HN_3, a previously unried precursor as the source of active nitrogen. A new, all-stainless steel apparatus which is UHV compatible, has been constructed. The apparatus has been constructed, tested and modified. Experiments have been carried out which show that gallium nitride and aluminium nitride can be made from the reaction of hydrazoic acid with trimethyl gallium and trimethyl aluminium respectively, at a hot substrate surface. Systematic studies aimed at producing high quality single crystal films have been made. The results are promising and uniform, golden yellow films of gallium nitride can now be produced. RHEED data show that the films are composed of highly orientated crystals. The X-ray results support this, with crystal sizes being at least 1000A with the crystals strongly orientated along the c-axis. There is however some evidence from ellipsometry that roughening of the layers occurs with increase in the thickness of the layer.

14. SUBJECT TERMS
Gallium nitride, epitaxial layers

15. NUMBER OF PAGES
12

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

TR-93-08

This report has been reviewed and is releasable to the National Technical Information Service (NTIS). At NTIS is will be releasable to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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Summary

This project has been primarily concerned with investigating a new approach to the synthesis of epitaxial layers of high purity gallium nitride. The new approach involves the use of hydrazoic acid, HN_3, a previously untried precursor as the source of active nitrogen . A new, all-stainless steel apparatus which is UHV compatible, has been constructed. It has been designed to allow growth studies to be made by the chemical beam epitaxy (CBE) technique or by low pressure metal organic vapour phase deposition (LPMOCVD) at pressures up to ca. 1mbar. During the grant period the apparatus has been constructed, tested and modified. Experiments have been carried out which show that gallium nitride and aluminium nitride can be made from the reaction of hydrazoic acid with trimethyl gallium and trimethyl aluminium respectively, at a hot substrate surface. *In-situ* RHEED patterns and *ex-situ* Auger spectra and X-ray diffraction data have been obtained. Systematic studies aimed at producing high quality single crystal films have been made. The results are promising and uniform, golden yellow films of gallium nitride can now be produced. RHEED data show that the films are composed of highly orientated crystals. The X-ray results support this, with crystal sizes being at least 1000Å with the crystals strongly orientated along the c-axis. There is however some evidence from ellipsometry that roughening of the layers occurs with increase in the thickness of the layer. Since ellipsometry can provide a means of *in-situ* monitoring of film quality, further work is being undertaken to develop this aspect which seems vital for control of the process, before continuing with the AlN/CaN growth programme.

INTRODUCTION

Single crystal gallium nitride is a wide band gap semiconductor (3.45 eV) which, if it could be made in a sufficiently pure state (both crystal and

chemical) would be important as a material for producing blue LED's. However, attempts to grow single crystal GaN as high purity epitaxial layers with carrier densities ~10^{16} cm^{-3} and high mobilities, have failed. Moreover only n-type material seems to be produced and there is some evidence that this is due to nitrogen vacancies within the crystal lattice (1). The majority of attempts to grow epitaxial GaN have used ammonia as the precursor and single crystal sapphire (0001) as the substrate. Some workers have used active nitrogen and the methods have ranged from molecular beam epitaxy to high pressure chemical vapour deposition. The majority of these methods have recently been discussed in review articles (2,3,4).

PROGRAMME OF RESEARCH

The approach has been to investigate the use of an alternative source of active nitrogen as a precursor. Thus the chosen molecule is hydrazoic acid HN_3. This meets some of the criteria for a precursor in that it is volatile (b.pt. 37°C) and can be prepared from readily available starting materials. Most importantly, it has the potential of containing at least one "active" nitrogen atom in each molecule and hence should be a much more efficient source of the group V element than the previously used molecules.

The project aims were therefore:

(1) to construct a versatile apparatus to allow film growth studies;

(2) to commission this apparatus for use with hydrazoic acid and gallium trimethyl, gallium triethyl and aluminium trimethyl;

(3) to make systematic growth studies to establish if these reactions can be used to produce GaN single crystal films;

(4) to monitor *in situ* any crystal growth by use of RHEED and gas phase reactions by mass spectrometry;

(5) to monitor film quality change using *in-situ* ellipsometry;

(6) to make electrical measurements of epitaxial layers in order to establish carrier densities and mobilities.

The first four of these objectives have been undertaken successfully and some progress has been made with *in-situ* ellipsometry monitoring. The quality of the GaN is not yet however of the standard to justify electrical measurements.

EXPERIMENTAL

A photograph of the completed apparatus which has been built in these laboratories during the grant period is shown in figure 1.

The apparatus has been constructed from stainless steel to UHV specifications. Oxygen-free copper gaskets have been used throughout. The two chambers and the associated gas lines can be baked at 200°C thus ensuring that base pressures of $<10^{-10}$ mbar are readily achieved. A primary consideration of the design has been to allow growth conditions, particularly total pressure, to be as flexible as possible. Thus the apparatus can be operated from a chemical beam epitaxy mode through to a low pressure chemical vapour deposition conditions at pressures of up to ca. 1 mbar. Pressure variation is achieved by alteration of gas flowrates and by adjustment of the valve between the sample preparation chamber and the cryo-cooled diffusion pump.

Heated platen and substrate

The heating method provided a particular set of problems and a great deal of research effort was required before an acceptable solution was achieved.

The design criteria for the heater were that it should:

(i) provide uniform heating over the substrate surface,

(ii) be capable of producing temperatures in excess of 1000°C at the substrate surface,

(iii) provide uniform heating rates and maintain control of any pre-selected substrate temperature to better than ±2°C.

Three designs were used:-

(a) The initial design made use of an array of external infrared heaters (halogen lamps) focused on the substrate via a 15 cm quartz window. Although temperatures of 700°C were obtained in preliminary tests, problems were encountered in achieving uniform and stable temperature heating. There was also a severe dissipation of power (and consequent heating) within the quartz window. Thus led on one occasion to cracking of the window and hence this approach was abandoned as unsuitable for the present application.

(b) The substantial modification which was next adopted is shown in figure 2. The substrate holder is part of the vacuum interface but is capable of being rotated through 360° and can be adjusted in the vertical direction. Both of these features are necessary to enable the RHEED patterns to be obtained. It was also necessary to be able to tilt in the horizontal plane to accommodate ellipsometry measurements. The substrate holder was heated radiatively using a resistively heated tungsten filament placed in close proximity (~ 1 mm) to the substrate holder as shown in figure 2. In order to minimize oxidation of the filament, the furnace chamber was kept under a vacuum of $< 10^{-2}$ mbar by means of a rotary diffusion pump. Tests showed that the required temperature of > 1050°C for the substrate holder was achieved. However the lifetime of the tungsten filaments was unacceptably short (3-8

hrs).

(c) The presently used and very reliable method has involved replacing the tungsten filament with a specially machined graphite block (see figure 2). Using this with the addition of a microprocessor controlled heating supply has eliminated the problems and provided both the necessary temperatures and a temperature control of ± 2°C. The graphite heater has operated for six months without a replacement being necessary.

There are six gas lines leading into the deposition chamber. Each has a filter, an on-off valve and a fine control valve for precise adjustment of flowrates. The lines are arranged for the introduction of $Ga(CH_3)_3$ or $Ga(C_2H_5)_3$, $A\ell(CH_3)_3$, nitrogen, hydrazoic acid, hydrogen and one (at present) spare line.

In-situ monitoring of both gaseous reactants and products can be made by means of a 0-300 a.m.u. quadrupole *mass spectrometer*. A compact ellipsometer (Optichem Ltd.) has been fitted so that *in-situ* film thickness and refractive index measurements can be made. A reflection high energy electron diffraction instrument (RHEED) is also installed so that *in-situ* measurements of crystal quality can be carried out

Hydrazoic acid is prepared *ex-situ* in a dedicated apparatus. The hydrazoic acid is stored in a stainless steel vessel and a diluent gas such as helium can be added as necessary. This container is then attached to one of the gas lines leading to the growth chamber.

The usual substrate for growth of epitaxial GaN is sapphire (0001). However, the lattice mismatch is 8.3%. In the case of silicon, this mismatch is reduced to 4.8%. There have, however, been reports that better quality GaN films can be produced by growing a buffer layer of AlN between the substrate and the gallium nitride (5). In this work silicon (100) and sapphire (0001)

and $(11\bar{2}0)$ surfaces have been used. These were cleaned by standard methods until the appropriate RHEED pattern was obtained from the substrate surface.

Results

(1) It was quickly established that gallium nitride films could be grown on all three surfaces.

(2) Provided that HN_3:$Ga(CH_3)_3$ ratio maintained with at least a 10:1 excess of the former, there was relatively little carbon incorporation in the surface layer (as established by *ex-situ* Auger spectroscopy).

(3) It was also possible to grow AlN films on sapphire using $Al(CH_3)_3$ instead of its gallium analogue.

(4) All films were strongly orientated polycrystalline materials as established by RHEED and *ex-situ* X-ray diffraction methods.

Systematic studies

A large number of growth experiments of GaN have been carried out over the temperature range 600-1200K primarily on the sapphire (0001) surface. A variety of HN_3:$Ga(CH_3)_3$ ratios in the range 5:1 to 30:1 were used. The aim was to establish the factors which determine whether single crystal or polycrystalline material is produced. Although single crystal GaN has not yet been grown, significant progress has been made towards determining the parameters necessary for achieving this end. In particular it has been established that the best films have been grown:

(a) with either a buffer layer of AlN or (so far equally successfully) with an initial buffer layer of 300-400Å of gallium nitride grown at a lower temperature (ca. 800K) than the main layer.

(b) substrate temperatures in the range 900-1200K seemed to have little influence on film quality.

(c) it was critical to have a uniform flow of the reactant molecules over the entire substrate surface. Any inhomogeneities lead to non-uniform film growth which was characterized by different coloured samples usually with interference fringes.

(d) as film thicknesses exceeded 2000Å there tended to be some roughening of the surface layer.

(e) the layers on silicon were significantly poorer than on sapphire and this work was stopped.

A RHEED photograph and X-ray diffraction spectrum for one of the best films are shown in figures 3 and 4 respectively. As can be seen in figure 3 there is some streaking of the RHEED pattern which is indicative of highly aligned polycrystalline material. The peak half-width in figure 4 is 14° (θ-2θ) which is considerably narrower and indicative of larger crystals than have been reported by other workers (6). Hence we believe it is possible to grow single crystal material from these starting materials (7).

Future work

The biggest handicap to more rapid progress is the time taken to make systematic studies using the present analysis methods. Much more rapid turn round of samples could be achieved if poor crystal quality could be detected at an early stage of growth. Hence conditions could be changed or the growth run aborted. The way to monitor this process at the growth temperature is by *in-situ* ellipsometry. However this is a technique which has rarely been used to follow growth processes and never with gallium nitride. Hence development work is necessary and this is being undertaken. The potential of the

technique can be seen from figure 5. In this figure the changes in the two characteristic angles are plotted and modelling calculations suggest a film of ~2μm has been produced. It is therefore believed that reliable ellipsometric data would greatly assist this project and hence at this stage, establishing the ellipsometer as a routine technique is being given the highest priority.

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Figure 1 VLPCVD apparatus

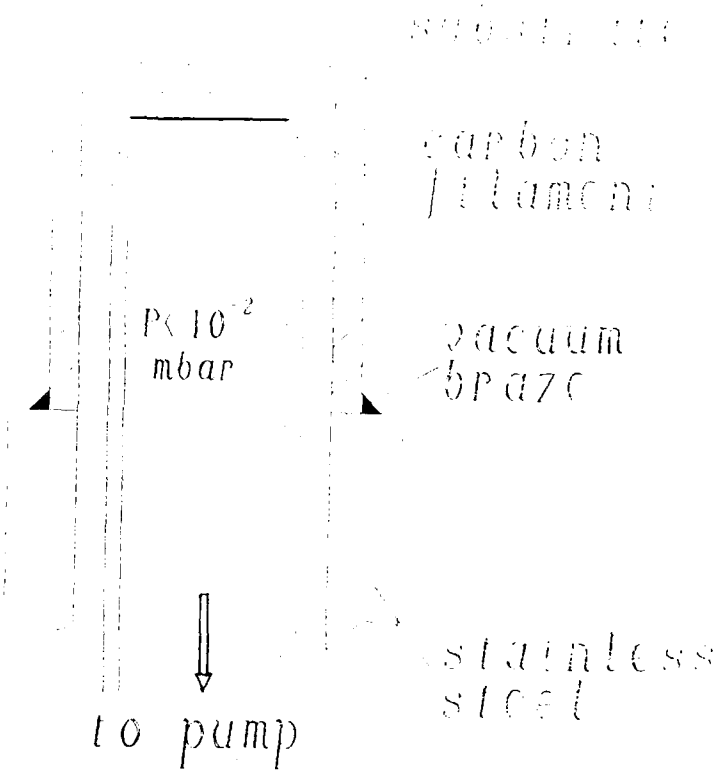

Figure 2 Schematic design for heated platen

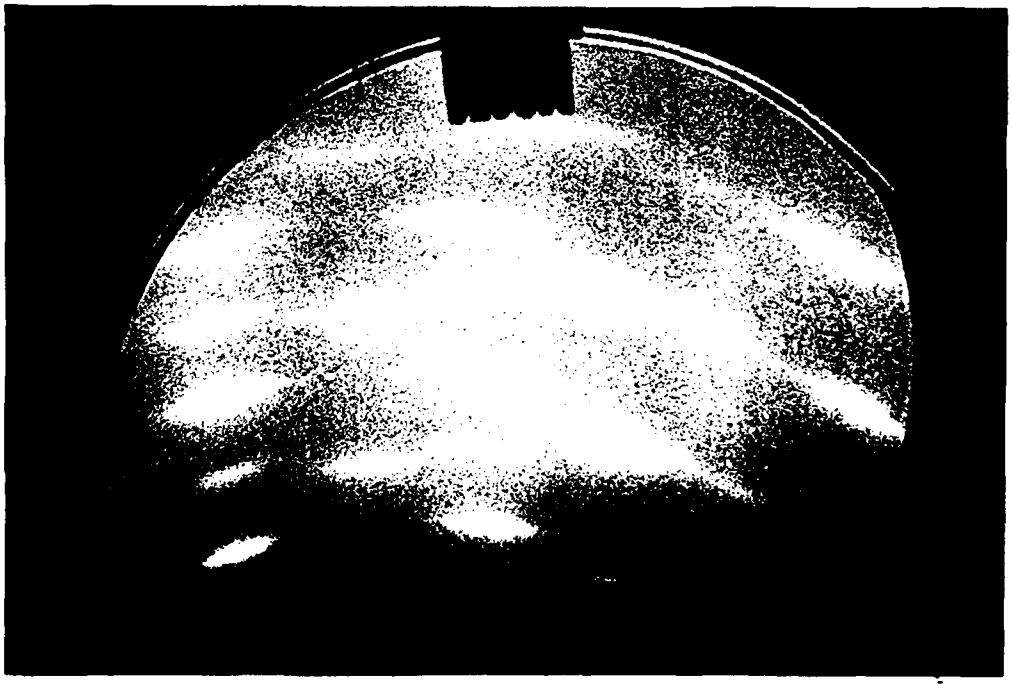

Figure 3 RHEED pattern for GaN on sapphire (0001)

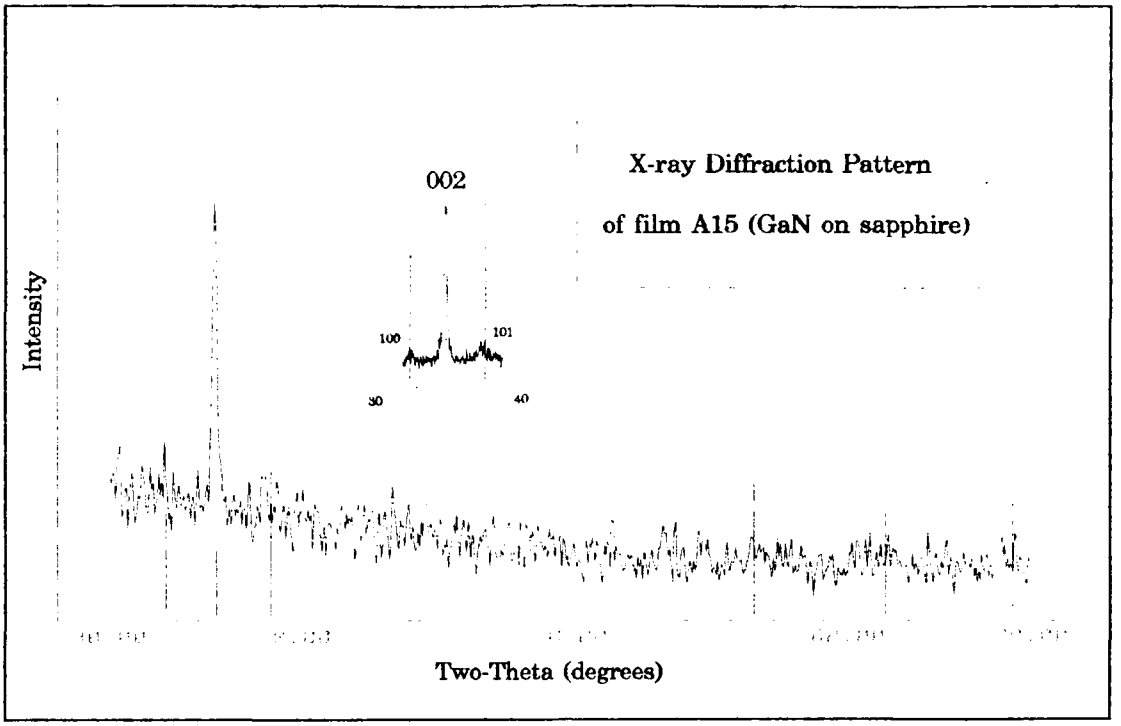

Figure 4 X-ray diffraction pattern for GaN on sapphire (001)

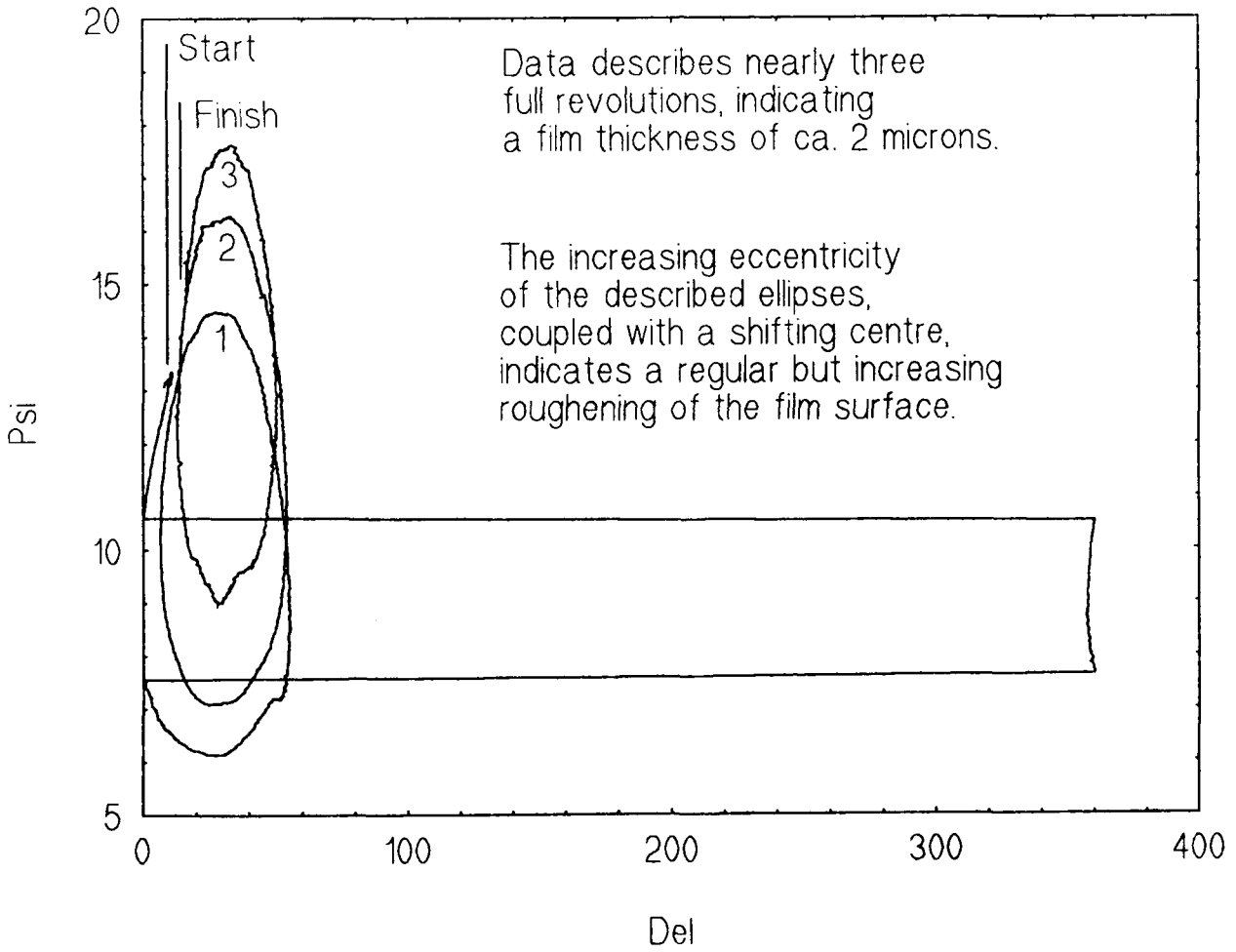

Figure 5 Ellipsometer trace of growth of GaN on sapphire (0001)